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## Research Article

# Novel Photocatalytic Reactor Development for Removal of Hydrocarbons from Water

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Hydrocarbons contamination of the marine environment generated by the offshore oil and gas industry is generated from a number of sources including oil contaminated drill cuttings and produced waters. The removal of hydrocarbons from both these sources is one of the most significant challenges facing this sector as it moves towards zero emissions. The application of a number of techniques which have been used to successfully destroy hydrocarbons in produced water and waste water effluents has previously been reported. This paper reports the application of semiconductor photocatalysis as a final polishing step for the removal of hydrocarbons from two waste effluent sources. Two reactor concepts were considered: a simple flat plate immobilised film unit, and a new rotating drum photocatalytic reactor. Both units proved to be effective in removing residual hydrocarbons from the effluent with the drum reactor reducing the hydrocarbon content by 90% under 10 minutes.

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## 1. INTRODUCTION

Hydrocarbons can contaminate the aqueous environment through several routes, for example, as by-products of the oil and gas industry such as drill cuttings, or as surface run off from petrol stations and garages. Pollution resulting from hydrocarbons [1, 2] contaminating the marine environment must be addressed due to the potential toxic effects associated with these compounds can cause considerable harm to a range of targets within the environment [3–5]. Produced water presents a significant environmental problem to the oil industry internationally. In one year over 8500 tonnes of oil was discharged from oil and gas installations to the North Sea from produced water discharges [6]. This is a particular problem now as the offshore industry is moving towards zero discharges from platforms.

Drill cuttings are one of the by-products of oil exploration and recovery, with around 8000 m<sup>3</sup> of diesel and low toxicity oil contaminated drill cuttings deposited around the base of platforms in the North Sea [7]. Drill cuttings consist of small pieces of rock which are generated when drilling a well, which vary in size from gravel to fine silt. These cuttings are carried from down hole to the oil platform by drilling fluid which not only lubricates and cools the drill

bit, but also prevents blowouts. On the platform, the cuttings are separated from the fluid with the fluid being reinjected. Most of the cuttings will also, at some point, come into contact with hydrocarbons which are difficult to remove in an environmentally friendly manner. In the past, almost all of the drill cuttings from the North Sea were dumped overboard onto the seabed.

Since the detrimental environmental impacts [8] of these cuttings were established, the government legislation has reduced the amount of drill cuttings permitted to be discharged into the sea and is moving towards banning the practice altogether [9, 10]. Consequently, the oil and gas industries have investigated alternative methods for disposing of drill cuttings. Processes that have been investigated include reinjecting the cuttings back into the well (well injection) [7] or shipping the cuttings to shore for treatment. The on-shore treatment and disposal options which include techniques such as thermal desorption, thermal distillation, solvent extraction, solidification, incineration/combustion, and landfill [11].

With thermal desorption [12], the drill cuttings are treated by heating the materials, which results in the vaporisation of water and hydrocarbons. This vapour is separated and subsequently recondensed giving an oil/water liquid and

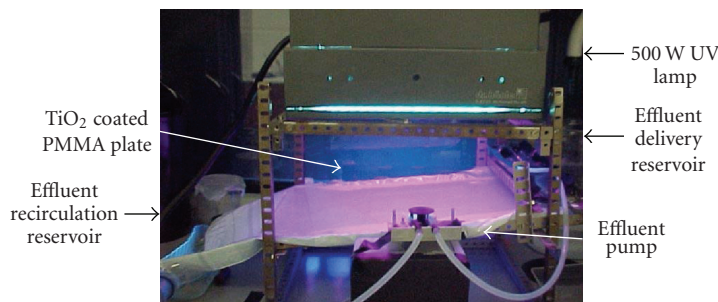


FIGURE 1: Prototype flat plate reactor treatment system under a UV source.

clean drill cuttings. The drill cuttings are then bagged and used for landfill whilst oil and water are separated. The recovered oil is burned in oil-fired power stations whilst the water is filtered to remove any residual hydrocarbons before being discharged into the sea. This water may still have residual hydrocarbon content.

Hydrocarbon contamination of water can also occur at the distribution stage as well as extraction. A particular example of such contamination results from “surface runoff” from Garage Forecourts. This effluent frequently contains petrol, diesel, oils, brake fluids, and also dust from brake parts and exhaust particles. The effluent is collected from drainage tanks for specialised treatment and disposal. Typically, the waste water effluent is passed through filtration systems but cannot fully remove volatile organic compounds (VOCs), and hence secondary treatment is often required.

Semiconductor photocatalysis is a rapidly developing process which may have a significant impact on the reduction and removal of these harmful and toxic compounds from produced water and waste water effluents and has even been used for potable water treatment [13–17]. This technology should be therefore a highly feasible process for the treatment of both produced waters and waste water runoff from garage forecourts. Although the use of the technology for removal of a vast range of compounds from water has been previously reported, one of the main challenges to date has been the up-scaling of the process to a size where it can practically treat large volumes of water. Many processes reported are usually treating litres per hour or even tens of litres per hour. Most practical effluent treatment processes require at least  $5\text{--}10\text{ m}^3\text{hr}^{-1}$ , and some offshore oil and gas platforms generate up to  $10^5\text{ m}^3\text{hr}^{-1}$ . A review by Alfano et al. [18] provides an excellent overview of many of the practical processes that have been developed for photocatalytic water treatment, particularly those utilising solar energy. In this paper, we report the development of both flat bed and drum reactor designs for the treatment of two real contaminated water samples, that is, a pretreated produced water and a waste water sample from a garage forecourt. The basic concept of these processes has been assessed and described herein.

In this paper, we describe a method of substituting the water filtration system, as an addition to the current system, to achieve very low levels of hydrocarbons in water.

## 2. MATERIALS AND METHODS

### 2.1. Multiplate thin film reactor design

There are several important parameters in the reactor design; one of the most significant of which is the active photocatalyst coating and the underlying substrate material. In addition, the coating preparation and the surface area of the catalyst available to the pollutant molecules are also crucial considerations. Two substrate materials were studied in this investigation: polymethylmethacrylate (PMMA) and titanium metal.

It is well known that certain forms of PMMA are transparent to ultraviolet radiation making the material ideally suited for an optical type chemical reactor where ultraviolet light is used to activate the photocatalyst. The other material under investigation is titanium. Although expensive, there is an important property in that when the titanium is oxidised, titanium dioxide is produced which is the photocatalyst being used in the reactor. There may also be advantages in that; there is likely to be good adhesion between the titanium and titanium dioxide.

The initial system developed for treating contaminated water was based on a thin film photocatalytic reactor. Figure 1 shows the prototype design of the photocatalytic reactor where the UV source was mounted on a support frame above the coated plate. The plate was placed on a water tight channel which had an effluent delivery tank at the head and an effluent collection reservoir at the base. The plate was mounted at an angle inducing effluent flow when introduced at the top of the unit.

The thin film plates of either PMMA or titanium were coated with  $\text{TiO}_2$  in a 50 mL methanol suspension, containing between 200 and 250 mg of photocatalyst. This was achieved by stirring the solution for 10 minutes to obtain an evenly distributed mixture; this was then applied to the PMMA or titanium plates. The plate to be coated was placed in a shallow vessel with the  $\text{TiO}_2$ /methanol solution applied centrally, and the vessel gently tipped from side to side to produce an even coating.

In this type of unit, the plates and plate reservoirs ultimately could be jointed creating a “concertina” multiple plate reactor module for large-scale water treatment (see Figure 2).

The contaminated water sample used to assess the efficiency of this reactor was a sample of effluent taken

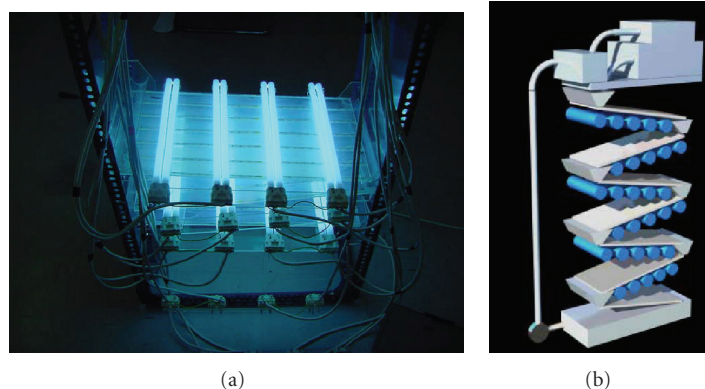


FIGURE 2: Multiple thin film plate reactor stack (a) lab-based unit, (b) concept design for scaled-up unit.

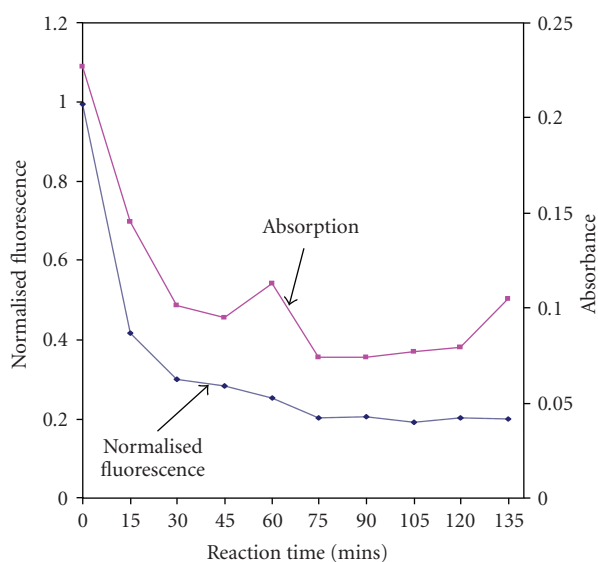


FIGURE 3: Demonstration of the decrease in both absorbance and fluorescence activity of produced water with reaction time.

from a thermal desorption plant used to treat drill cuttings. The water sample typically contained 100–200 ppm hydrocarbons. This is significantly higher than the permissible discharge consent level for the UK controlled waters which is currently 30 mg/L [19].

We have previously reported the use of fluorescence spectroscopy for in situ monitoring of hydrocarbons in the marine environment. As part of this study, the applicability of absorption spectroscopy as an alternative technique to fluorescence spectroscopy was assessed. Figure 3 shows the results obtained for the analysis of a produced water sample using absorption and fluorescence spectroscopy, when the sample was treated using a flat plate reactor. As can be seen from the figure for this study, a good correlation between the two techniques was obtained and hence absorption spectroscopy was used for monitoring the hydrocarbon reduction for this investigation. The analysis was performed using a Novaspec II absorption spectrometer monitoring the decrease of the broadband peaking at 335 nm.

## 2.2. Drum reactor design

The drum reactor was designed to be a single pass continuous flow system for produced water/effluents. If after one pass the water was still above the discharge level for hydrocarbons, the water was allowed to run into a lower reservoir. Typically, the residence time in each drum was just over 3 minutes, with a total treatment time after passing through three drum modules being around 10 minutes. If at this stage the sample was still contaminated, it was then recirculated.

The addition of hydrogen peroxide to the photocatalytic system has been previously reported to enhance photocatalytic degradation rates through the generation of additional OH radicals via the conductance band reaction with the peroxide molecule [20, 21]. This was also found to be the case for the degradation of hydrocarbons in both our systems so was introduced into the final reactor setup. The hydrogen peroxide concentration was 0.5% v/v total concentration in the effluent. This recirculation process was continued until the hydrocarbons had been removed.

The  $\text{TiO}_2$  utilised in the reactor was a Hombikat C material supplied by Sachtleben Chemie, Duisburg, Germany. The reactor drums were irradiated using 36 W Philips PL-L sun-lamp UV tubes supplied by RS Components Ltd, Northants, UK. Figures 4(a) and 4(b) show the patented photocatalytic drum reactor configuration [22]. Sampling was achieved via the open air vents at the fluid inlet side of the reactor drum.

The waste water sample was taken from an interceptor waste water collecting effluent from a Garage Forecourt. This sample contained a mixture of hydrocarbons at a total COD level of between 3500 and 4000 ppm.

The destruction of the hydrocarbons was monitored by both measuring the chemical oxygen demand of the sample and also by gas chromatography/mass spectrometry (GCMS) using a Hewlett Packard model 5890 series II GC connected to a Hewlett Packard model 5971A mass selective detector.

## 3. RESULTS AND DISCUSSION

### 3.1. Flat plate reactor

Initial experiments focused on the optimisation of the  $\text{TiO}_2$  coating on the plate substrate were performed by preparing

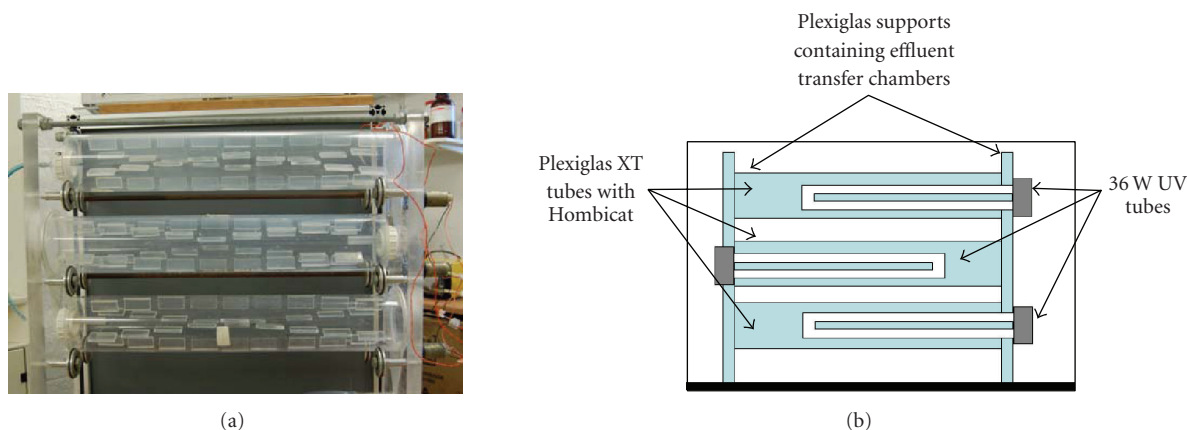


FIGURE 4: (a) Photocatalytic reactor drum setup with patented paddle design [20] and (b) drum reactor configuration in UV box.

different coatings using the slurry method described above. It can be seen from Figure 5 that the most effective coatings were achieved using suspensions of between 200 and 250 mg of  $\text{TiO}_2$  (Degussa P25) in 50 mL of pure methanol followed by air drying at room temperature. Experiments were also carried out using elevated temperatures for evaporating off the methanol. As can be seen from Figure 5, the effect of catalyst loading on the system was only marginal, which would be expected in this type of unit where mass transfer kinetics would be expected to predominate [23–25].

After establishing loading parameters, the reaction rate was studied as a function of plate angle and substrate material. It can be seen from the plot that the PMMA substrate plate consistently outperformed the titanium substrate when both are coated with the optimal  $\text{TiO}_2$  loading at a sub  $15^\circ$  angle. The primary reason that the shallower plate angle had greater destructive efficiency is most likely due to a greater contact time of the effluent on the catalyst plate due to the slower flow rates and hence longer residence time (see Figure 6).

To determine increase in efficiency of the reaction by the addition of an alternative electron acceptor to oxygen (air), hydrogen peroxide solution was added at an optimum initial concentration of 0.5% to the produced water sample. Figure 7 shows the results of bubbling air only through the produced water, using a combination of air and hydrogen peroxide and hydrogen peroxide only. It can be seen that a significant enhancement was obtained with the addition of the peroxide alone. In addition bubbling air through this system did not lead to any additional enhancement of the destruction of the hydrocarbons in the produced water. This supports similar observations previously reported by our own group and others [26–31] and indicates that the rate of aeration of the solution by ambient air is faster than the rate of oxygen consumption associated with the photocatalytic destruction of the hydrocarbons.

### 3.2. Drum reactor

Initial experiments using the drum reactor were configured for continuous flow effluent treatment. The photocatalyst

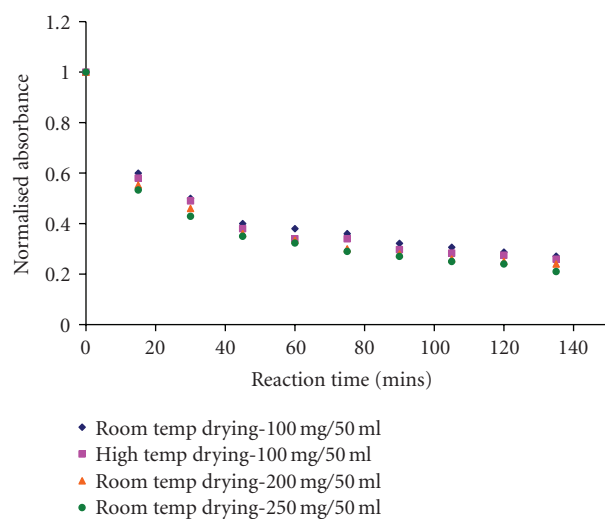


FIGURE 5: Comparison of  $\text{TiO}_2$  loading and heat treatment.

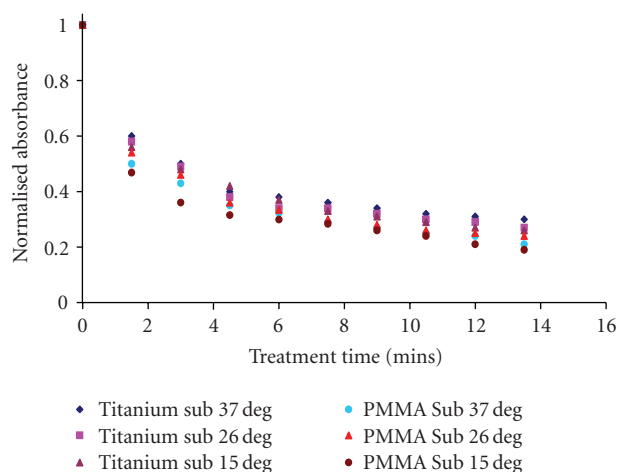


FIGURE 6: Comparison of substrate material with reactor plate angle at the optimum  $\text{TiO}_2$  loading.

was initially washed with distilled water to remove excess particulates  $\text{TiO}_2$  from the surface of the pellets which



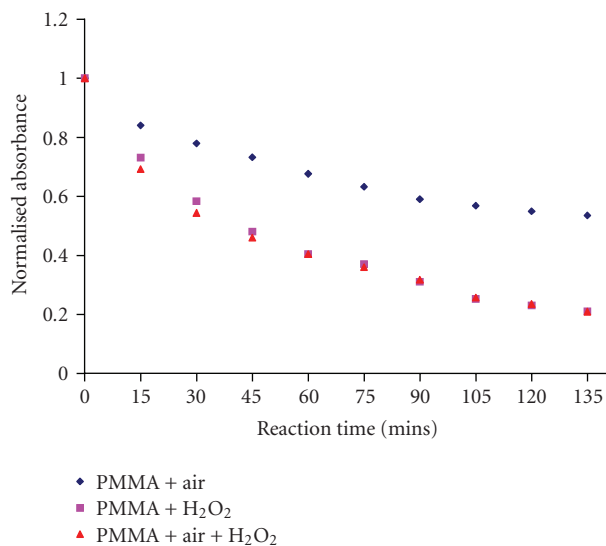


FIGURE 7: Effect of bubbling air and adding hydrogen peroxide on the destruction rate of produced water with the plate reactor.

TABLE 1: Mean COD values for pretreatment, 1st pass and 2nd pass through the drum reactor.

Sample pass	Mean COD mg/L
0 pass pretreatment	3618
1st pass through drum reactor	2166
2nd pass through drum reactor	868

could affect the photocatalytic reaction by providing a higher surface area of catalyst within the reactor drum. This would also cause secondary problems for the setup of the reactor as the excess particulates could block the effluent transfer pathways.

Figure 8 shows the GC/MS results which clearly show a 90% overall destruction over 10 minutes of VOCs present in the waste water effluent treated through a total of 600 g of the TiO<sub>2</sub> catalyst. This was achieved by passing the waste water effluent through three consecutive reactor drums each containing 200 g loads of photocatalyst. It can be seen that with 10 minutes and after passing through the third drum, the level of hydrocarbons in the water sample had virtually disappeared.

The chemical oxygen demand (COD) of the water samples was also measured as an indicator of the total hydrocarbon level in the untreated and treated samples. Table 1 shows the mean COD values obtained from 5 experimental runs with each point being an average of 3 samples. It can be seen that the COD value decreases very quickly during the time it takes to process through the 3 consecutive reaction drums (10-minute reaction time). As these experiments were performed on different days and the waste water effluent was decanted from a large storage drum, it is possible that the effluent content was not 100% consistent.

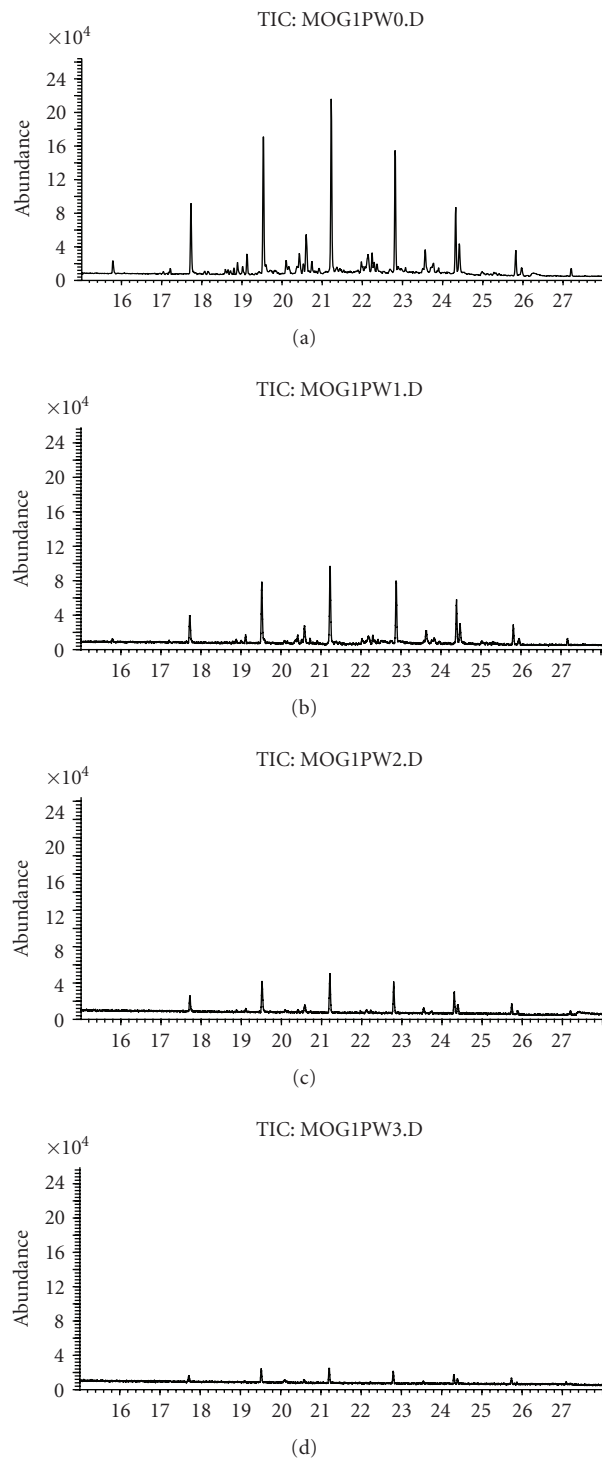


FIGURE 8: GC/MS chromatogram of waste water effluent, (a) pure sample with no treatment, (b) 1st pass through drum reactor, (c) 2nd pass through drum reactor, and (d) 3rd pass through drum reactor (accumulative total) catalyst treatments over a 10-minute irradiation.

#### 4. CONCLUSION

The results of this study have demonstrated that both reactor designs proved effective for the removal of hydrocarbon

contamination from waster water effluents. With the thin film plate reactor, the assessment of PMMA and titanium metal plates as substrate materials was investigated under different conditions. By varying the mounting angle of the plates, the PMMA plate mounted at 15 degrees produced 60% destruction after 15 minutes. This demonstrated that the lower plate angle increases the retention time of the pollutant and therefore the chance of a successful catalyst–pollutant interface. An investigation into the effect of adding air and  $\text{H}_2\text{O}_2$  to the system showed that the addition of air alone to the reactor produced 40% degradation, compared to the 80% degradation of  $\text{H}_2\text{O}_2$ , over 135 minutes.

With the development of the pelletised  $\text{TiO}_2$ , it was possible to develop an alternative reactor configuration with a smaller foot print. Conventional powder catalyst systems have traditionally posed removal problems with filtration, and settling is required to remove powder from the effluent. This limits the type of reactor design to batch, as it is impractical to provide online filtration for a continuous flow reactor system.

The drum reactor reported in this study was configured for continuous flow through 3 reactor tubes (see Figure 4(b)) each containing the same quantity of catalyst; GC/MS results showed the effective 90% removal of VOCs over 5 minutes. The mechanical mixing action of the paddle array within the reactor tubes greatly increases the pollutant-catalyst interface, enhances mass transport, and also removes the need for additional air to be added to the system. The patented paddle array also maintains an even spread of the catalyst pellet within the drum which would normally suffer from “corkscrew” effect of the turning drum. Using a standard indicator for organic compounds in water, chemical oxygen demand, the drum reactor showed an 85% reduction of organic content.

It should finally be noted that for both reactors assessed in this paper, the processes had been developed as “polishing” units and a complementary technology to existing techniques. The technique would not be viable for more heavily contaminated water samples as the kinetics of the process would require very significant reaction times and the photocatalytic process cannot compete with existing technologies, where semiconductor photocatalysis has demonstrated a particular effectiveness in such a final polishing step for removal of more resilient compounds that traditional waste water technologies are not capable of removing.

## ACKNOWLEDGMENT

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